

Conference materials

UDC 53.097

DOI: <https://doi.org/10.18721/JPM.153.251>

Ruthenium as an electrode material for the fast electrochemical actuator

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Abstract. Electrolysis of water performed by alternating polarity (AP) voltage pulses increases the operating frequency of the electrochemical actuator by several orders of magnitude due to the fast recombination of the produced gas. The gas is collected in nanobubbles that disappear quickly due to spontaneous combustion of hydrogen and oxygen. However, this type of electrolysis damages the electrodes and the actuator performance deteriorates with time. Platinum electrodes suffer from mechanical action of nanobubbles, while titanium structures are oxidized. A promising material is ruthenium due to its chemical inertness and mechanical strength. In this work, we test Ru, Pt and Ti electrodes in the AP electrolysis. The degree of wear, current flowing through the cell, and threshold voltage are analyzed and compared.

Keywords: alternating polarity electrolysis, nanobubbles, electrodes, ruthenium, degradation

Funding: The study was supported by RSF, grant 18-79-10038.

Citation: Shlepakov P. S., Uvarov I. V., Svetovoy V. B., Ruthenium as an electrode material for the fast electrochemical actuator, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 15 (3.2) (2022) 280–284. DOI: <https://doi.org/10.18721/JPM.153.251>

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Материалы конференции

УДК 53.097

DOI: <https://doi.org/10.18721/JPM.153.251>

Рутений как материал электродов быстрого электрохимического актюатора

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Аннотация. Электролиз воды, выполняемый микросекундными импульсами напряжения переменной полярности, повышает рабочую частоту электрохимического актюатора на несколько порядков вследствие быстрой рекомбинации произведенного газа. Газ производится в виде нанопузырьков, которые быстро растворяются в результате спонтанной реакции горения водорода и кислорода. Однако электроды быстро разрушаются под механическим воздействием нанопузырьков, в то время как титановые электроды окисляются. Перспективным материалом является рутений, обладающий



высокой химической инертностью и твердостью. В данной работе выполнено сравнение рабочих характеристик рутениевых, платиновых и титановых структур в электролизе переменной полярности.

Ключевые слова: электролиз биполярными импульсами, нанопузыри, электроды, рутений, деградация

Финансирование: Работа выполнена при финансовой поддержке РФФ, проект № 18-79-10038.

Ссылка при цитировании: Шлепаков П. С., Уваров И. В., Световой В. Б. Рутений как материал электродов быстрого электрохимического актюатора // Научно-технические ведомости СПбГПУ. Физико-математические науки. Т. 15. № 3.2. С. 280–284. DOI: <https://doi.org/10.18721/JPM.153.251>

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Introduction

Electrochemical production of gas in a closed chamber provides extra pressure that pushes a flexible membrane up. This phenomenon is used as a working principle for the electrochemical actuators [1], which are good candidates for various microfluidic systems. Conventional actuators based on the DC electrolysis suffer from a long response time due to slow recombination of the produced gas [2]. The use of microsecond AP voltage pulses instead of DC voltage solves the problem. The chamber is filled with nanobubbles (NBs) with a diameter of 100 nm, which disappear in milliseconds due to spontaneous combustion of hydrogen and oxygen. A fast electrochemical actuator was demonstrated, which works several orders of magnitude faster than conventional devices [3]. However, the electrodes of the actuator have a limited lifecycle because of two factors. The first one is a strong mechanical action of NBs on the electrode surface, while the second factor is the oxidation of the electrode material. Platinum electrodes are not oxidized, but are destroyed quickly by the mechanical action of NBs [4] due to a relatively low hardness of Pt (3.5 units on Mohs scale) [5]. Titanium is much harder material (6 units), but it is prone to oxidation that reduces the current flowing through the electrolyte and suppresses the gas production [6]. A promising electrode material is ruthenium. It has high hardness of 6.5 units and a conductive oxide. The resistivity of poor ruthenium is $7.1 \mu\Omega\cdot\text{cm}$, while RuO_2 demonstrates a comparable value of $35 \mu\Omega\cdot\text{cm}$ [7]. These properties allow one to expect that Ru electrodes withstand the mechanical action of NBs and can be oxidized without significant decrease of the gas production. In this work, we investigate the degradation of Ru electrodes in the AP electrolysis in comparison with Pt and Ti structures.

Materials and methods

The electrodes of the concentric shape (see Fig. 1,*a*) are fabricated on a silicon wafer with $0.9 \mu\text{m}$ SiO_2 layer grown by thermal oxidation in wet oxygen. The electrode material is deposited by magnetron sputtering. The sample is placed in a Petri dish filled with the electrolyte, which is a molar solution of Na_2SO_4 in distilled water. A layer of SU-8 protects the signal lines from the electrolyte. Square AP voltage pulses are generated by a homemade generator and applied to the working electrode, while the other one is grounded. It was shown that the degradation of the electrodes goes slower at a higher frequency of pulses f [6]. Here we use $f = 500 \text{ kHz}$ that is the upper limit of the generator.

The samples are tested in two regimes. In the first one, the pulses with an amplitude of 11 V are applied continuously during 30 min. The voltage is not large enough to produce explosion of a microbubble, so the electrode surface is affected only by NBs. The experiment is performed at 100 nm thick Pt and Ru electrodes, as illustrated in Fig. 1,*b*. The current flowing through the electrochemical cell is recorded every 10 s by an oscilloscope Pico-Scope 5000 and the average absolute value I_{av} is calculated. SEM investigation of Ru electrodes is performed by SEM Zeiss

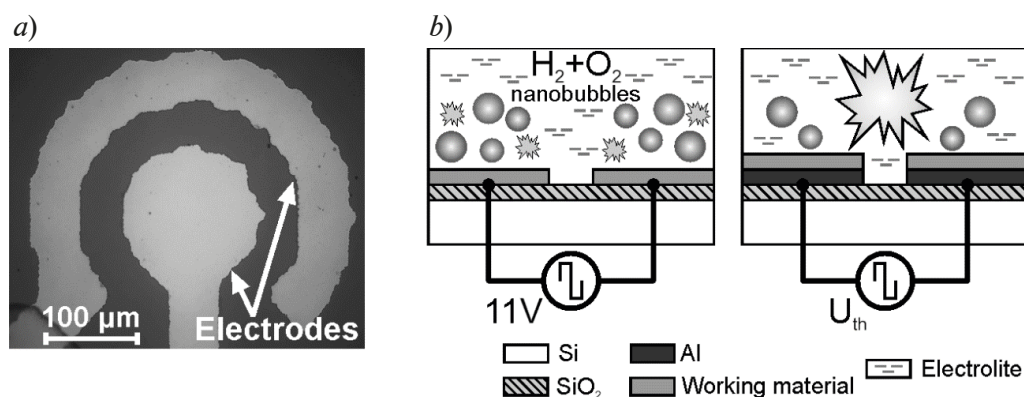


Fig. 1. Photograph of the electrodes, top view (a); schematic illustration of the continuous (left) and explosive (right) testing regimes (b)

Supra 40. Chemical composition is measured by energy dispersive X-ray (EDX) spectrometer Oxford Instruments INCA X-act at the acceleration voltage 6 kV.

In the second regime, the amplitude is adjusted to the threshold level U_{th} , at which the concentration of NBs in the electrolyte reaches a critical value. The NBs merge into a microbubble, which explodes with the release of a large amount of energy, as shown in Fig. 1, b. AP pulses are applied to the electrodes every 2 s until one explosion happens. The current drop in the cell during the explosion is tracked by our generator and voltage pulses stopped automatically. It sets the same conditions for each sample. The experiment lasts until no explosion happens during the 0.5 s of the AP pulses applying or the U_{th} reaches 19 V, which is the maximal voltage of the generator. The lifecycle and durability are investigated for Al/Ti and Al/Ru electrodes with a thickness of 500/100 nm. Aluminium layer is included to reduce electrical resistance of the signal lines.

Results and discussion

The time dependence of the current for Ru and Pt electrodes in the continuous regime is shown in Fig. 2, a. At the beginning of the test, the samples demonstrate similar I_{av} of 35.0 and 32.5 mA, respectively due to close values of electrical resistivity. Then I_{av} for Pt decreases as a result of the electrode damage. At the 13th minute the central electrode is almost completely destroyed as shown in Fig. 2, b, which is accompanied by a drop of the current. At the same time, Ru electrodes demonstrate a slight increase in the current throughout the test. The reason for the increase is the heating of the electrolyte and the chip. The damage is not observed, as one can see in Fig. 2, b.

SEM investigation of Ru electrodes revealed nanoparticles appeared on the surface after the electrolysis. Their concentration is higher at the edge of the electrode than at the central part.

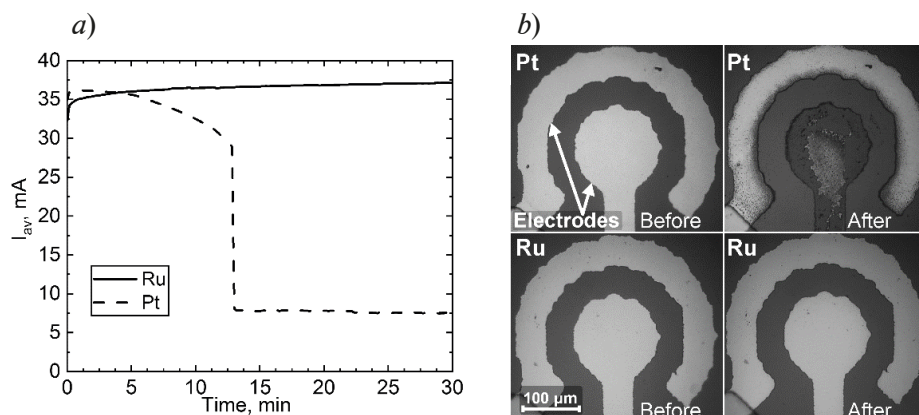


Fig. 2. The results of continuous test: time dependence of the current flowing through the electrodes (a); photographs of the electrodes before and after the test (b)

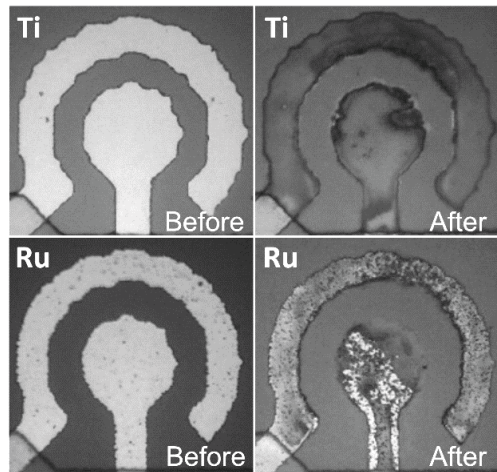


Fig. 3. Ti and Ru electrodes before and after the explosive test

EDX analysis shows the oxidation of the electrodes. The process goes faster at the edge because of higher current density. As was expected, the oxidation of Ru electrodes does not reduce the current due to metallic conductivity of ruthenium oxide.

In the explosive regime, Ti and Ru electrodes have an initial threshold voltage of 12-13 and 10-11 V, respectively. Ti electrodes darken due to oxidation (see Fig. 3), and U_{th} reaches the limit value of 19 V in 18 min. Ruthenium structures generate explosions during 2 hours. The threshold voltage increases to 12 V because of mechanical damage by explosions, and the test continues until the fatal destruction of the central electrode. Thus, Ru structures exhibit several times longer lifecycle compared to Ti samples. This result makes Ru a preferable material for the fast electrochemical actuator.

Conclusions

Ruthenium electrodes are tested in the electrochemical process performed by AP voltage pulses with the frequency of 500 kHz. In the continuous regime, Ru and Pt structures are compared. The platinum sample demonstrates high current in the beginning of the test, but I_{av} falls to the minimal value in 13 min due to mechanical damage by NBs. At the same time, the ruthenium electrodes provide a slightly increasing current due to heating of the electrolyte and do not show signs of wear. Ruthenium layer is oxidized in the electrochemical process, but this effect does not reduce the current due to a high conductivity of the ruthenium oxide. In the explosive mode, Ru and Ti electrodes are compared. Titanium structures start to produce explosions at $U_{th} = 12$ V. The maximal voltage is reached in 18 min because of oxidation, and the test is stopped. Ruthenium electrodes generate explosions at the pulse amplitude of 10-12 V and operate more than 6 times longer than Ti structures. The limiting factor is the significant damage of the central electrode by explosive microbubbles. Based on the results obtained, Ru is considered a preferable electrode material for the fast electrochemical actuator.

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Received 14.07.2022. Approved after reviewing 19.07.2022. Accepted 08.09.2022.